

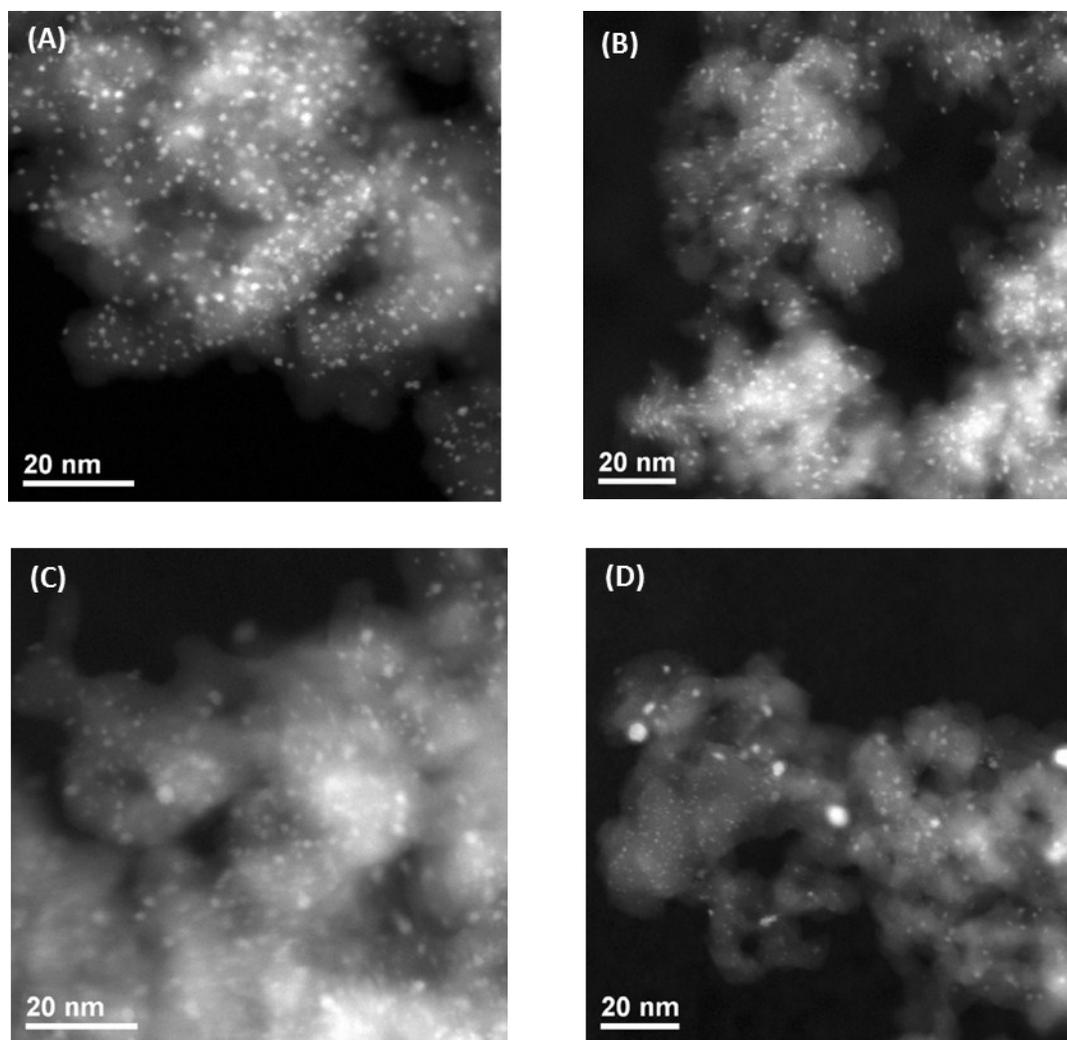
## Supporting Information

### **In situ, operando studies on size and structure of supported Pt catalysts under supercritical conditions by simultaneous synchrotron-based x-ray techniques**

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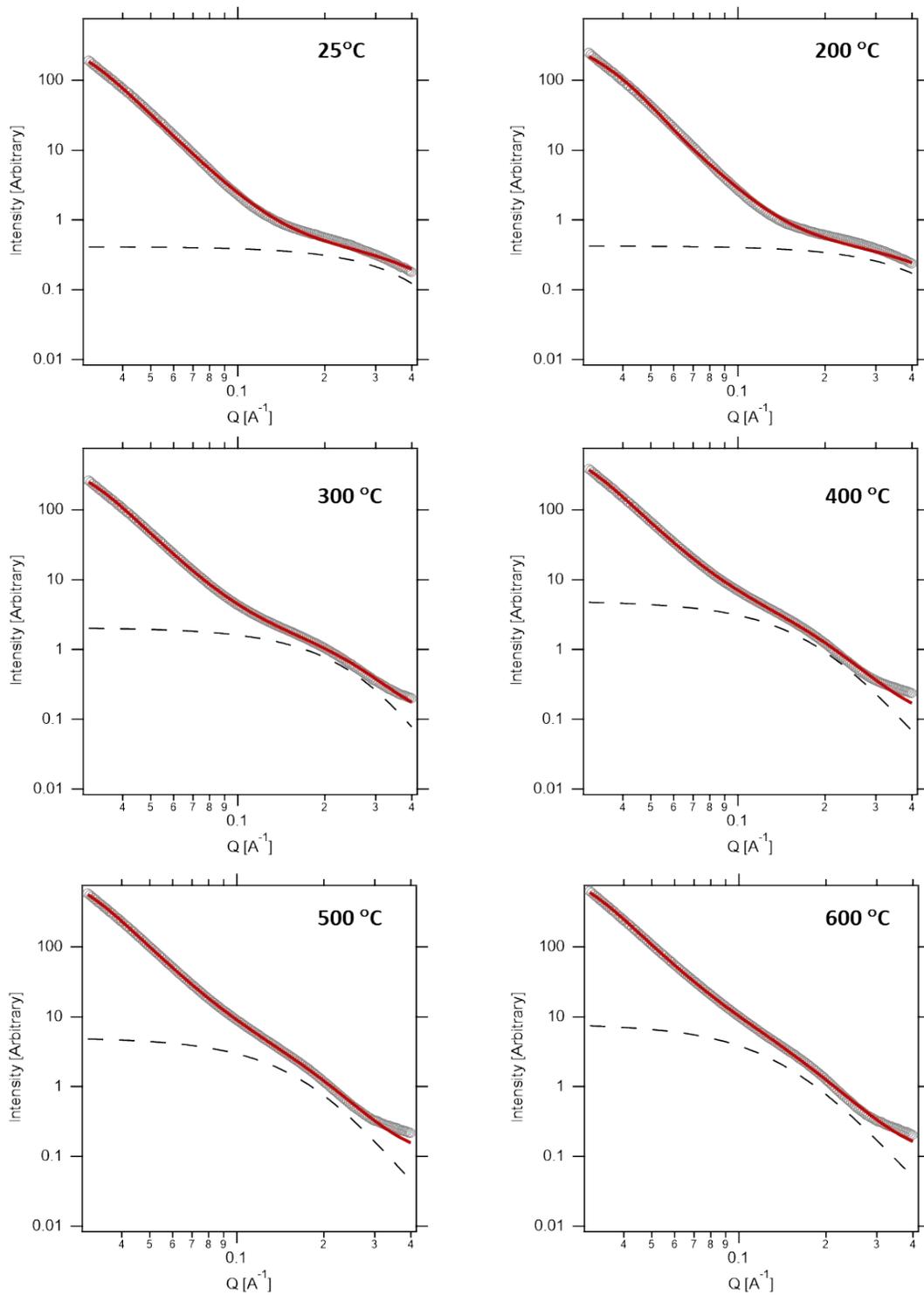
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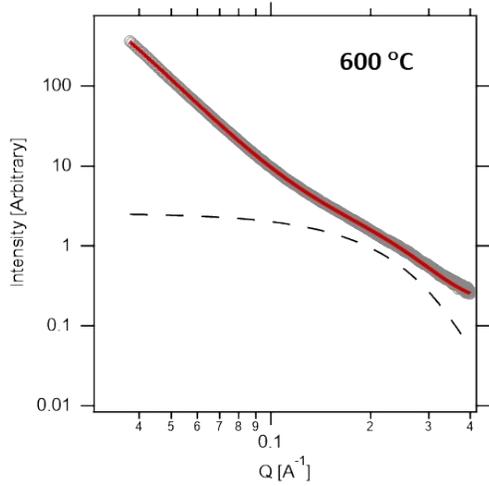
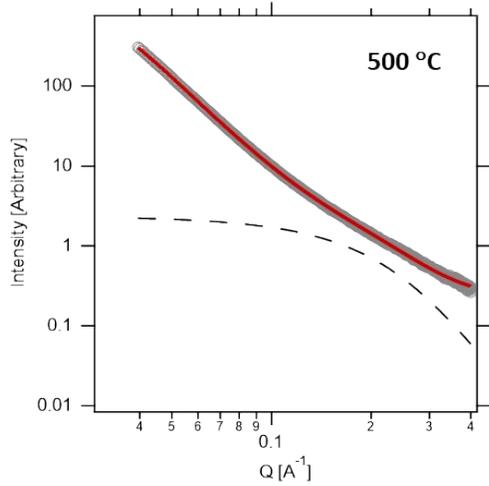
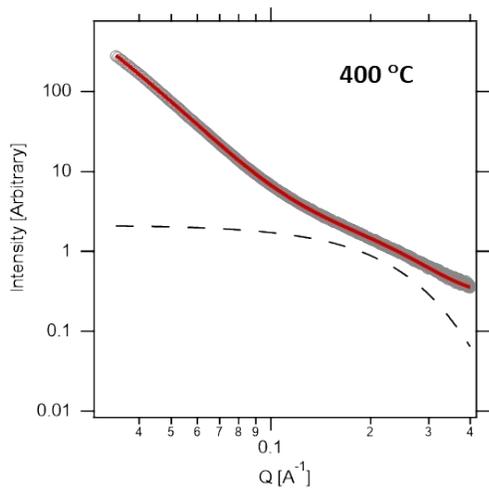
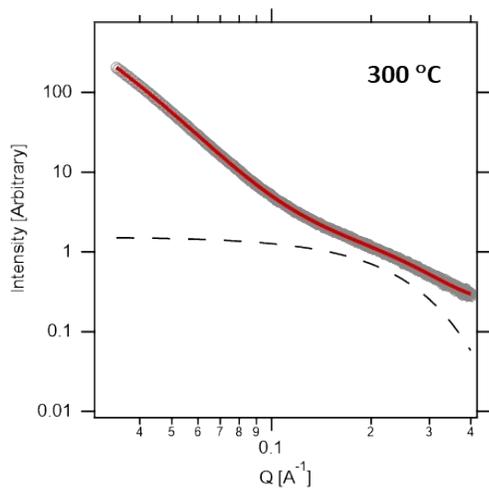
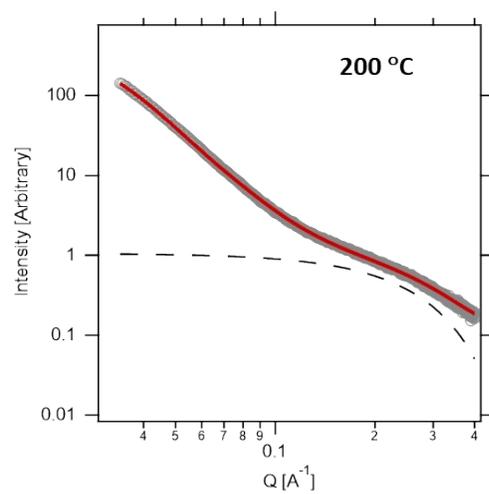
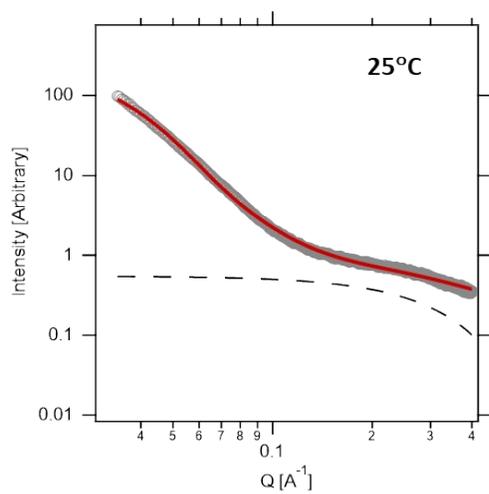
**Figure S1.** STEM images of Pt-Sn/SiO<sub>2</sub> catalysts, (A) Pt (B) Pt<sub>3</sub>Sn<sub>1</sub> (C) Pt<sub>1</sub>Sn<sub>1</sub> (D) Pt<sub>1</sub>Sn<sub>3</sub>

**Figure S2.** The fitting results of SAXS profiles of Pt, Pt<sub>3</sub>Sn<sub>1</sub>, Pt<sub>1</sub>Sn<sub>1</sub>, and Pt<sub>1</sub>Sn<sub>3</sub> obtained from the model curve fitting with Schultz-Zimm distribution : Red line shows the fitted result, gray circles indicates the raw data, and the dashed lines shows the model curve. The broad scattering below 0.1 Å<sup>-1</sup> is from support material (SiO<sub>2</sub>).

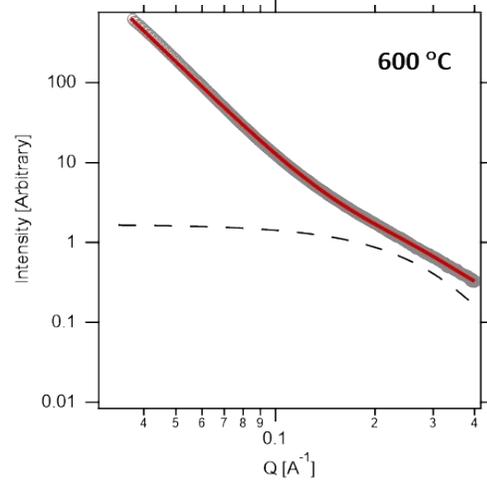
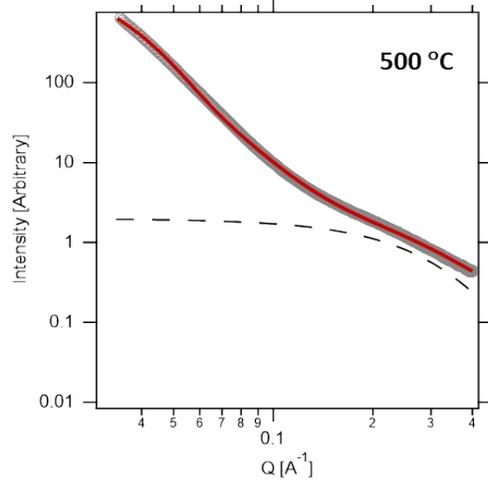
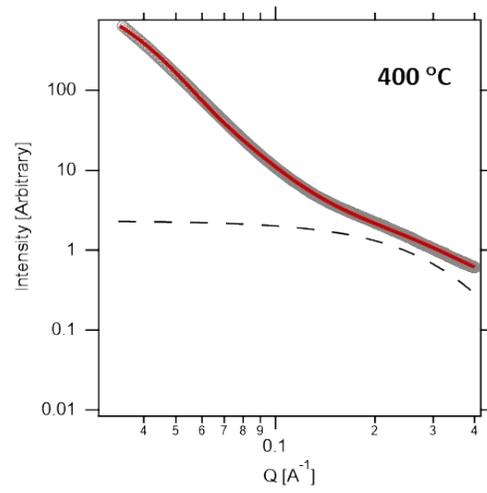
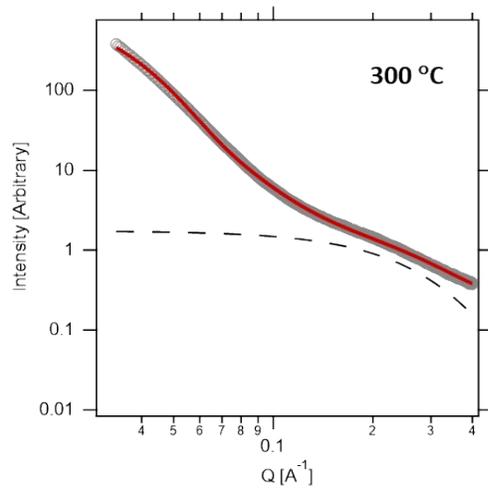
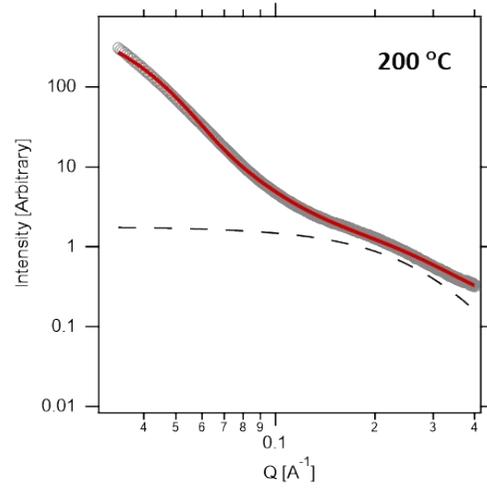
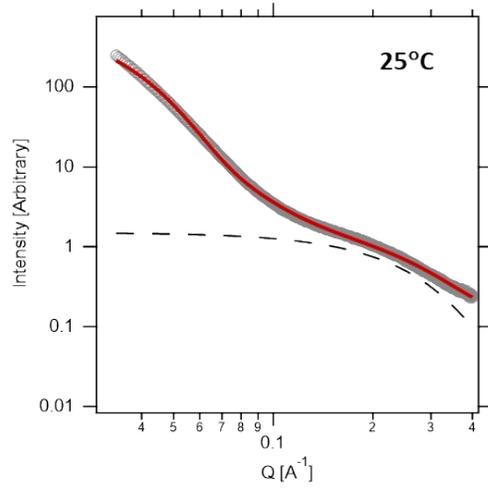
(a) Pt



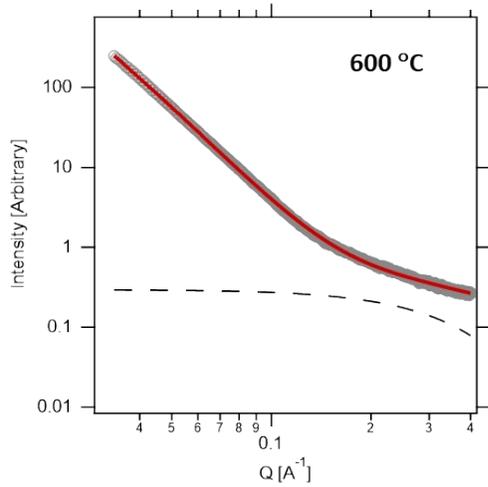
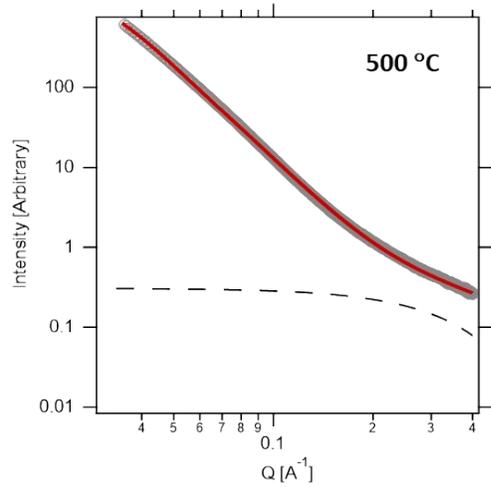
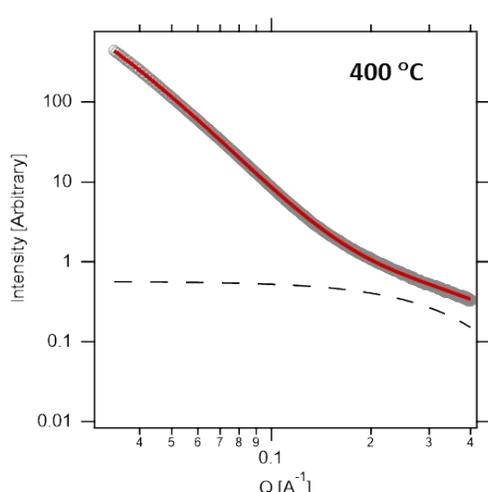
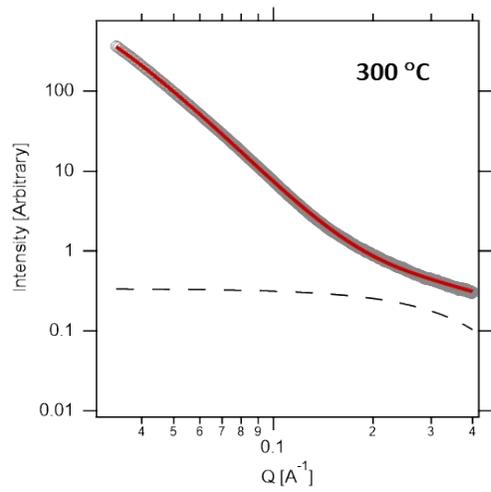
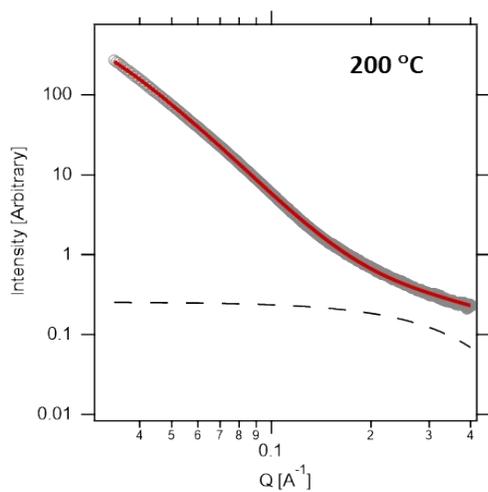
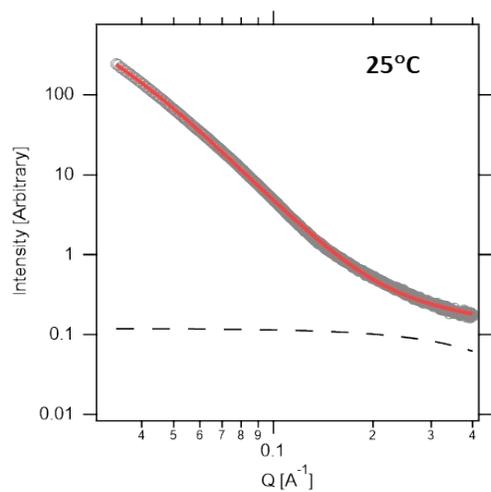
(b)  $\text{Pt}_3\text{Sn}_1$

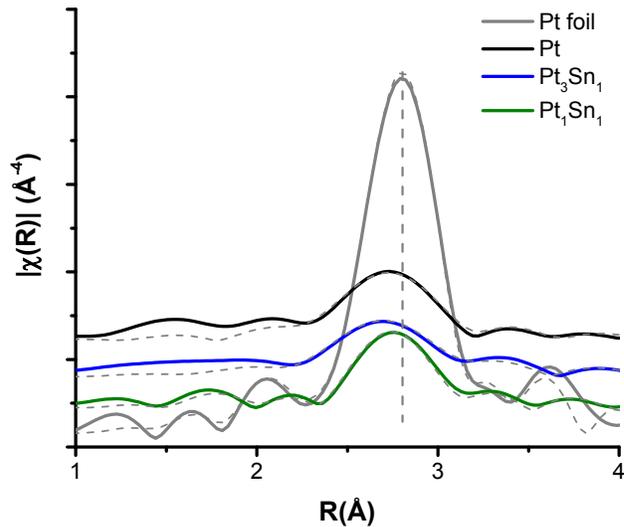


(c) Pt<sub>1</sub>Sn<sub>1</sub>



(d) Pt<sub>1</sub>Sn<sub>3</sub>





**Figure S3.** Fourier transform magnitude of the Pt L3 data and fit ( $k^3$  weighed) of  $\text{SiO}_2$  supported Pt,  $\text{Pt}_3\text{Sn}_1$ ,  $\text{Pt}_1\text{Sn}_1$  and Pt foil with a vertical offset added for clarity.

**Table S1.** Structural parameter determined from EXAFS analysis of Pt and Pt-Sn/ $\text{SiO}_2$  catalysts.

	Pt/ $\text{SiO}_2$	$\text{Pt}_3\text{Sn}_1/\text{SiO}_2$		$\text{Pt}_1\text{Sn}_1/\text{SiO}_2$	
	Pt-Pt	Pt-Pt	Pt-Sn	Pt-Pt	Pt-Sn
N	$7.2 \pm 0.9$	$4.9 \pm 1.2$	$0.7 \pm 0.3$	$5.6 \pm 0.7$	$0.8 \pm 0.2$
R (Å)	2.70	2.70	2.59	2.71	2.58
$\sigma^2$ (Å <sup>2</sup> )	$0.01 \pm 0.001$	$0.007 \pm 0.002$	$0.007 \pm 0.002$	$0.007 \pm 0.002$	$0.007 \pm 0.002$
$\Delta E$ (eV)	5.6	3.6	-0.6	3.5	3.5
R factor	0.0088	0.0069		0.010	

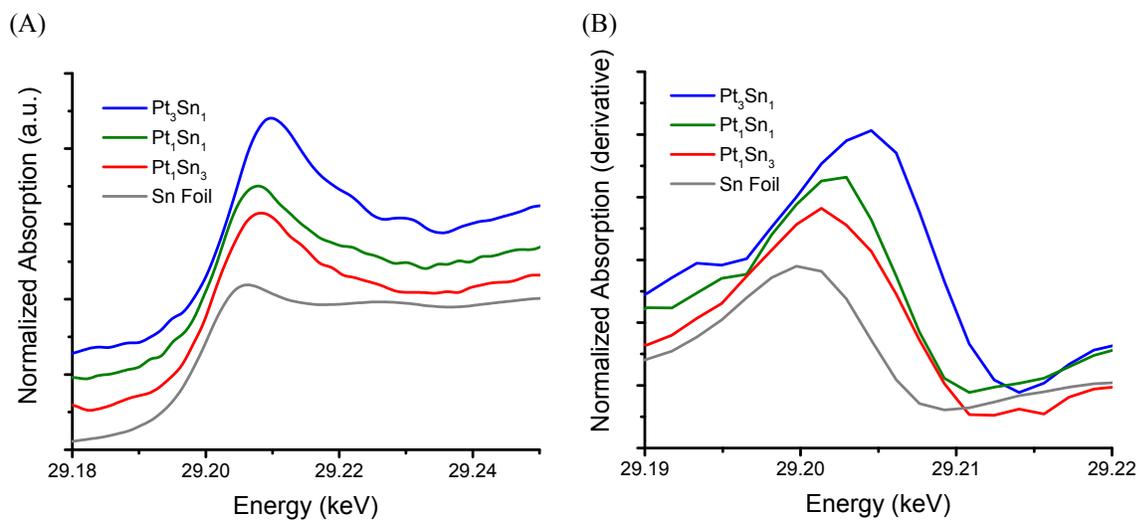
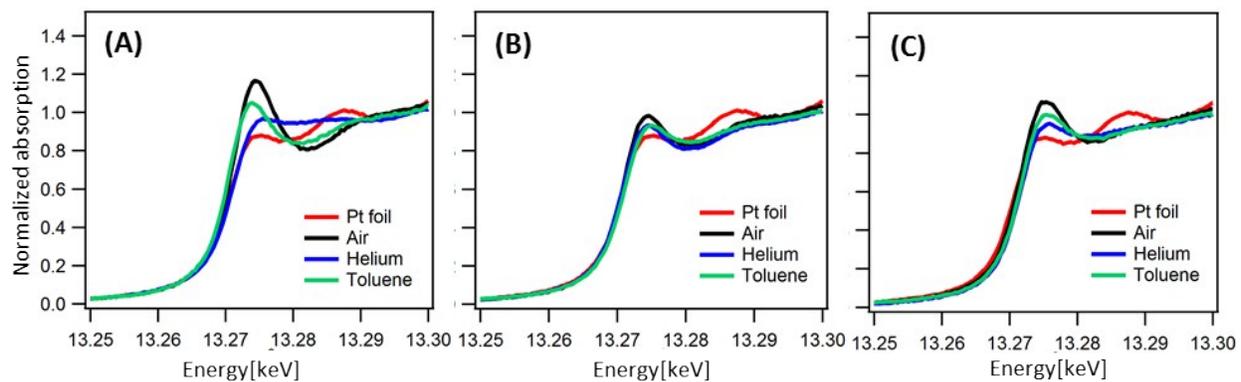
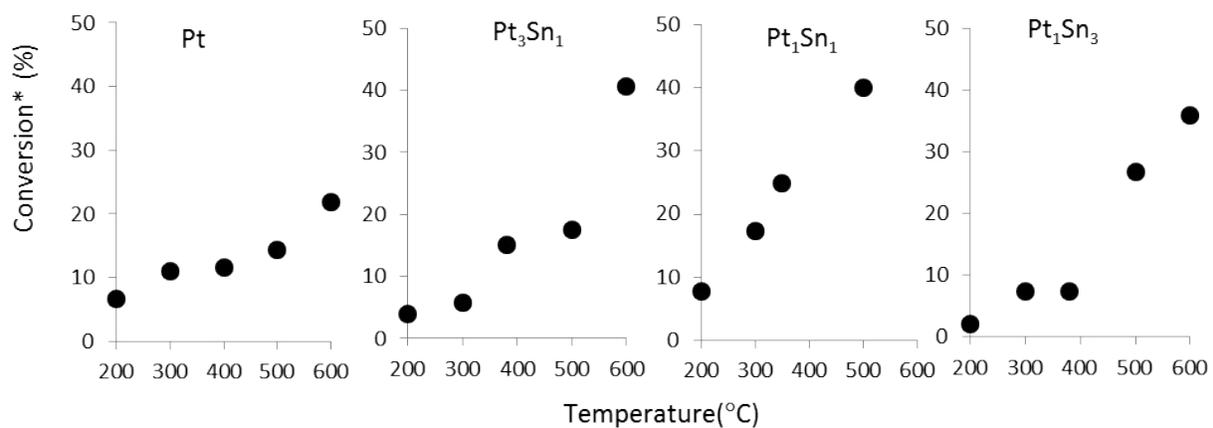


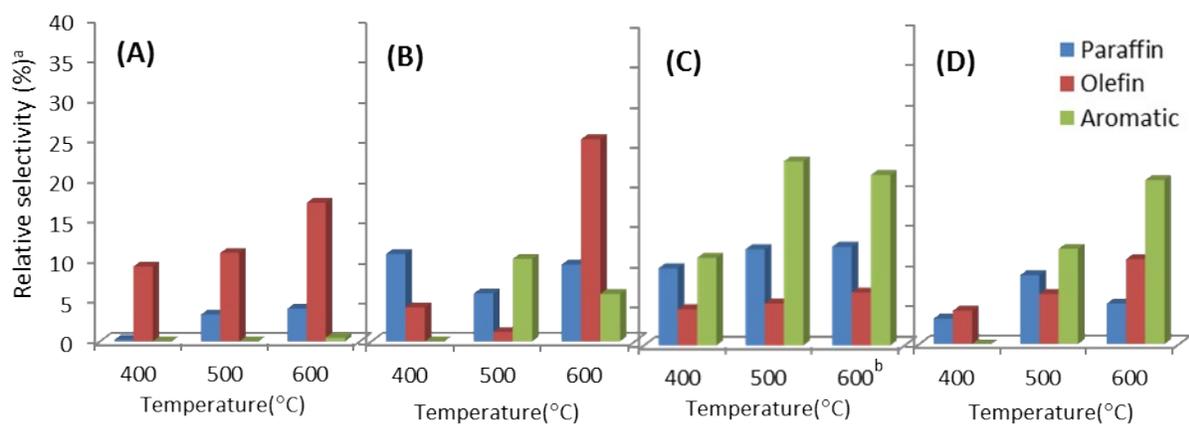
Figure S4. XANES spectra of (A) normalized Sn K-edge and (B) derivative plot of SiO<sub>2</sub> supported Pt<sub>3</sub>Sn<sub>1</sub>, Pt<sub>1</sub>Sn<sub>1</sub>, Pt<sub>1</sub>Sn<sub>3</sub> and Sn foil with a vertical offset added for clarity



**Figure S5.** Pt L<sub>2</sub> XANES for Pt-Sn/SiO<sub>2</sub> catalysts in air, Helium and the presence of toluene with respect to Pt foil. (A) Pt (b) Pt<sub>1</sub>Sn<sub>1</sub> (C) Pt<sub>1</sub>Sn<sub>3</sub> (Pt<sub>3</sub>Sn<sub>1</sub> is not shown)



**Figure S6.** n-dodecane conversion measured over Pt-Sn/SiO<sub>2</sub> catalysts under supercritical conditions (\*normalized with Pt)



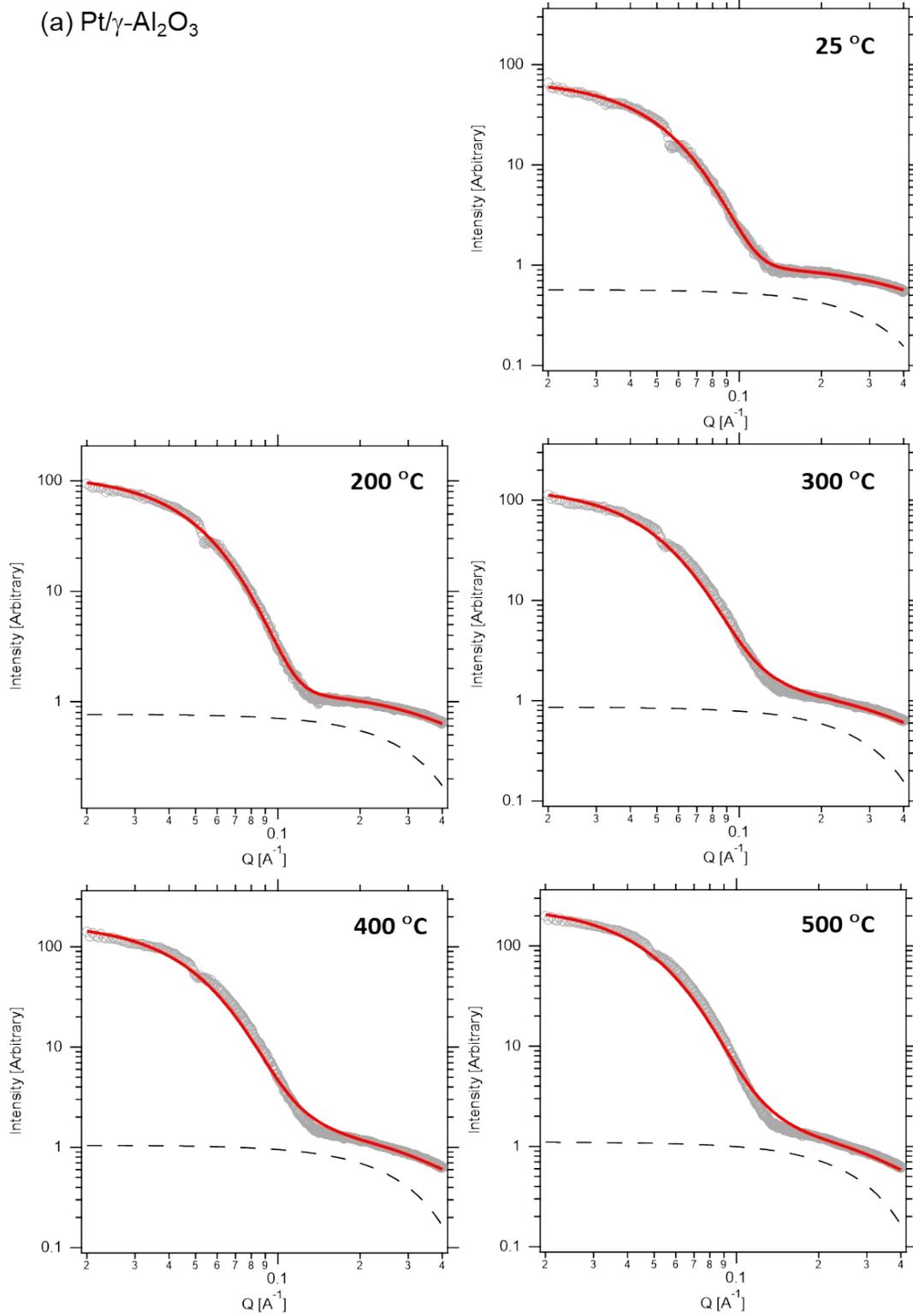
**Figure S7.** Catalytic selectivity of Pt-Sn/SiO<sub>2</sub> catalysts in the temperature range of 400 – 600 °C at 750 psi with n-dodecane; (A) Pt (B) Pt<sub>3</sub>Sn<sub>1</sub> (C) Pt<sub>1</sub>Sn<sub>1</sub> (D) Pt<sub>1</sub>Sn<sub>3</sub> (<sup>a</sup> normalized with conversion yields; <sup>b</sup> normalized by conversion yields at 500 °C)

**Table S2.** Products of n-  
Pt<sub>3</sub>Sn<sub>1</sub>/SiO<sub>2</sub> catalysts at

dodecane cracking over  
600 °C under 750 psi.

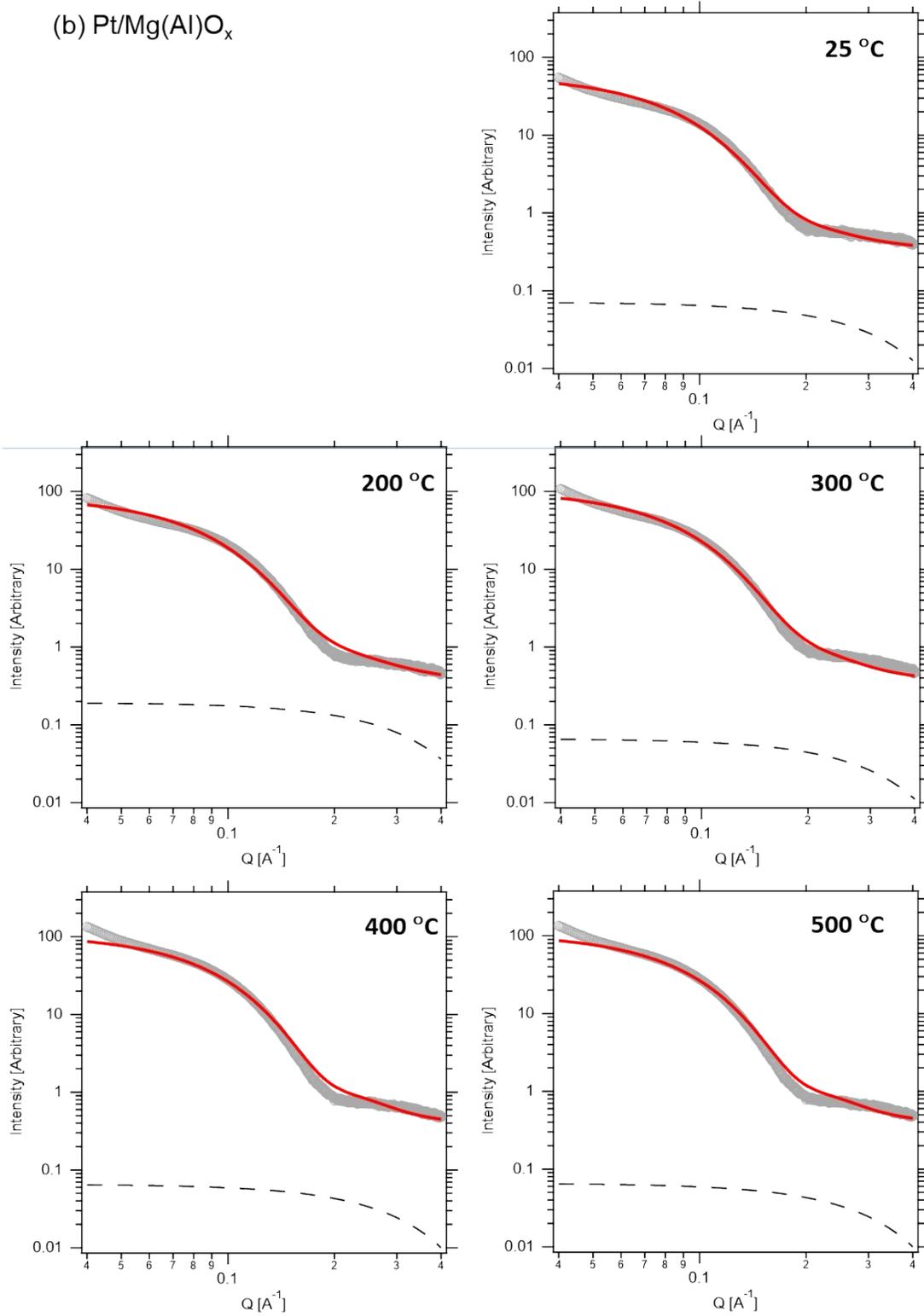
Time(min.)	Products
1.661	2-Hexene
1.796	3-methyl-cyclopentane
1.897	Methyl-cyclopentane
1.954	Benzene
2.081	1-Heptene
2.134	Heptane
2.251	2-Heptene
2.348	Methyl-cyclohexane
2.5	4-methyl-cyclohexene
2.634	Dimethyl-cyclopentane
2.785	Toluene
3.04	1-Octene
3.163	Octane
3.263	2-Octene
3.606	1,6-dimethyl-cyclohexene
3.769	1-ethyl-cyclohexene
4.307	Ethylbenzene
4.47	Xylene
4.899	1-nonene
4.993	o-xylene
5.094	Nonane
5.243	2-nonene
6.5	Propylbenzene
6.713	1-ethyl-2-methylbenzene
7.499	1-decene
7.586	Trimethylbenzene
7.736	Decane
7.907	4-decene
8.148	2-decene
8.78	Cyclopropylbenzene
10.263	Alkylbenzene
10.403	1-undecene
10.651	Undecane
12.089	Alkylbenzene
12.515	Methyl-undecane
12.998	IS
13.335	dodecane
13.996	dodecene
16.319	Tridecane

**Figure S8.** The fitting results of SAXS profiles of (a) Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (b) Pt/Mg(Al)O<sub>x</sub> as well as (c)Pt/SiO<sub>2</sub> obtained from the model curve fitting with Schultz-Zimm distribution : Red line shows



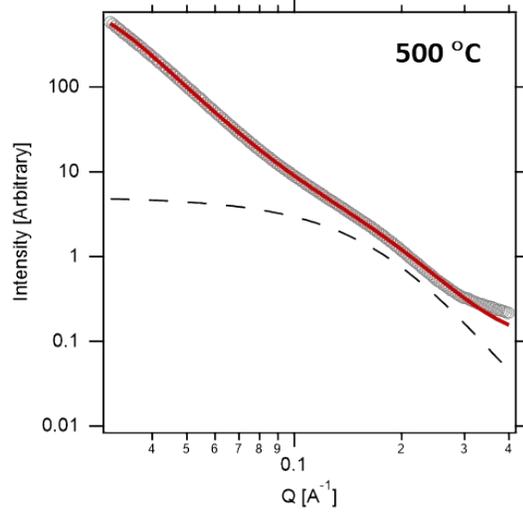
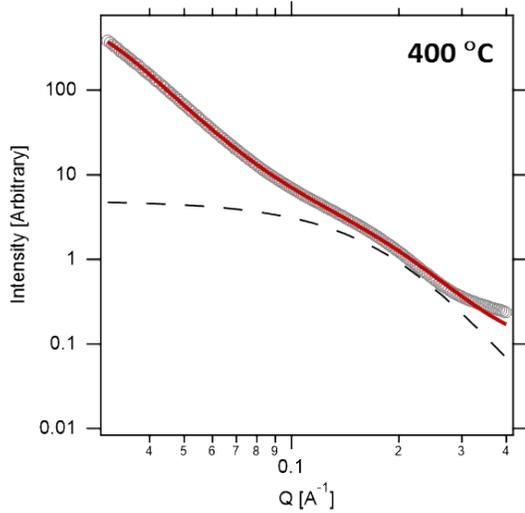
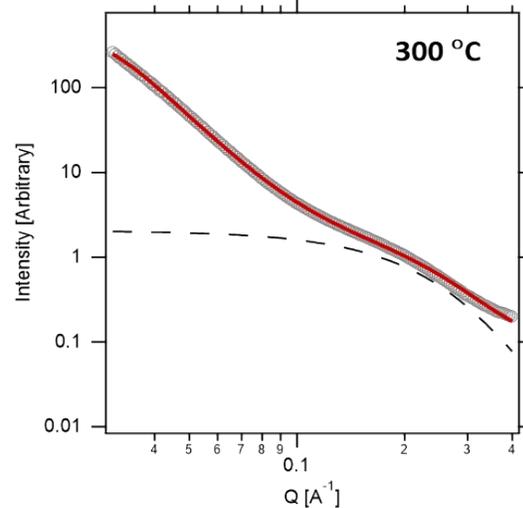
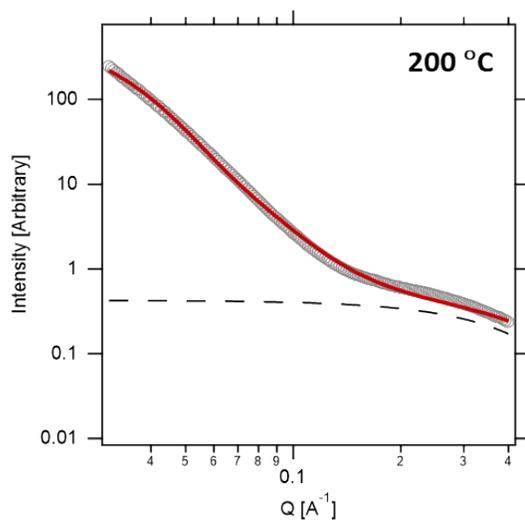
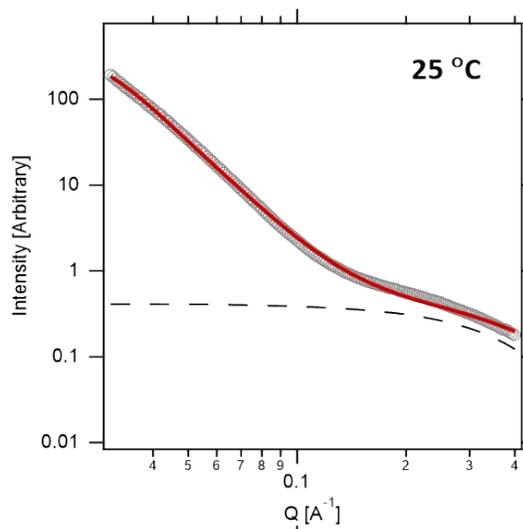
the fitted result, gray circles indicates the raw data (background subtracted), and the dashed lines shows the model curve.

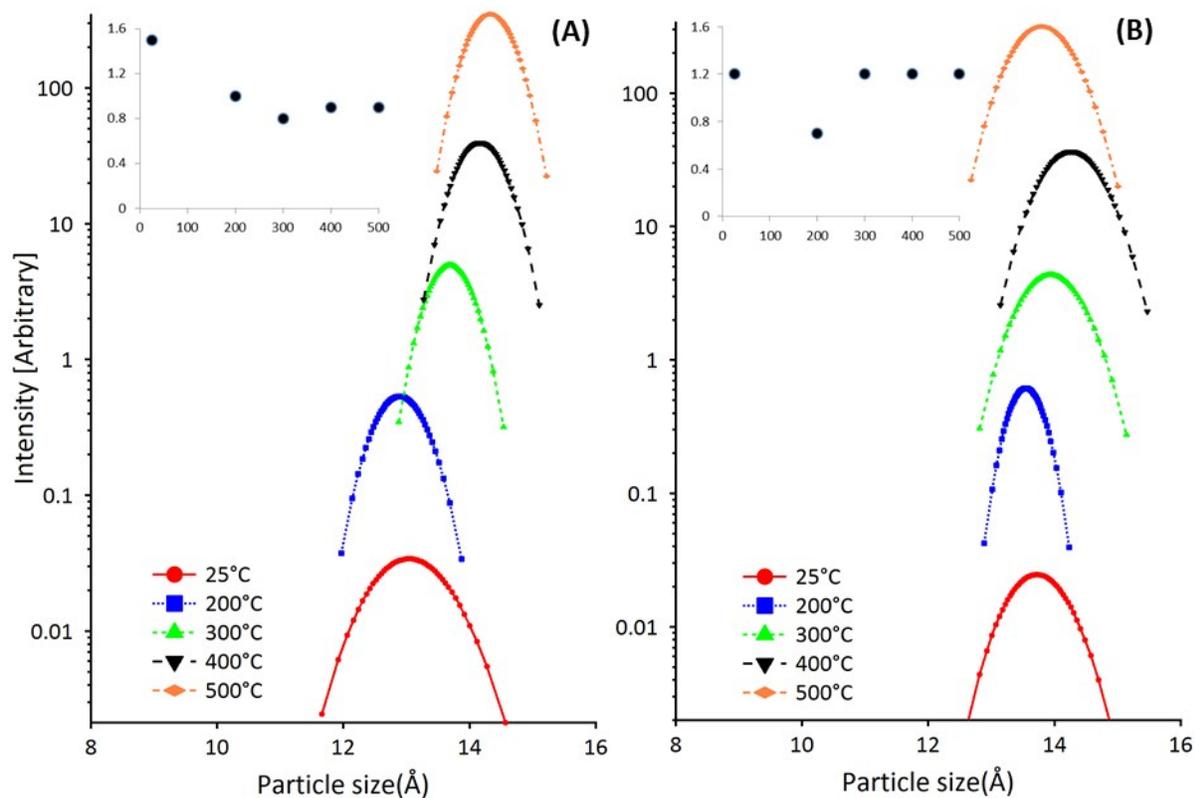
(b) Pt/Mg(Al)O<sub>x</sub>



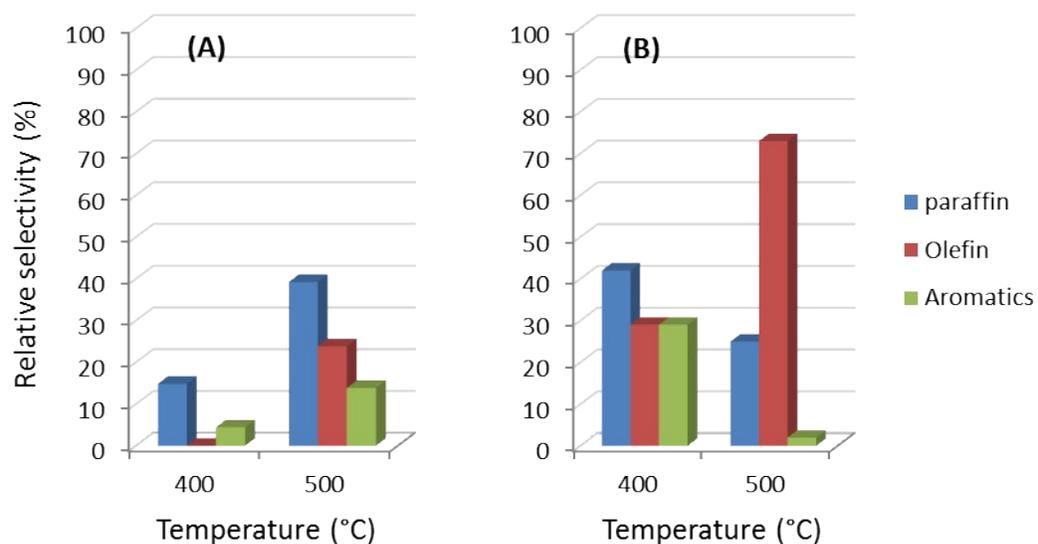


(c) Pt/SiO<sub>2</sub>





**Figure S9.** Size distribution profiles of Pt catalyst supported on (A)  $\gamma\text{-Al}_2\text{O}_3$  and (B)  $\text{Mg}(\text{Al})\text{O}_x$  in the temperature range of 25 to 500 °C at 750 psi with n-dodecane. Inset shows the corresponding FWHM values of catalysts.



**Figure S10.** Catalytic selectivity<sup>a</sup> of Pt catalyst supported on (A)  $\gamma\text{-Al}_2\text{O}_3$  and (B)  $\text{Mg}(\text{Al})\text{O}_x$  in the temperature range of 400 – 500 °C at 750 psi with n-dodecane (<sup>a</sup>normalized with conversion yield)